

Summary Abstract: Adsorption of cyclohexane on Ru(001): A high resolution electron energy loss and UV-photoemission study^{a)}

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The adsorption of cycloparaffins on metal surfaces is of particular interest since the vibrational spectra obtained with EELS (high resolution Electron Energy Loss Spectroscopy) for cyclohexane adsorbed on both Ni(111) and Pt(111) show two sets of C-H stretching modes.¹ One observed frequency range (2900–3000 cm⁻¹) compares well with the gas-phase spectrum obtained with IR and Raman spectroscopy,² whereas the observed C-H “soft” mode (2590–2720 cm⁻¹) was ascribed to an electronic interaction between some of the hydrogen atoms in the molecule and the metal surface, similar to the interaction which occurs in hydrogen bonding.¹ The adsorption of cyclohexane on the Ru(001) surface was studied by Madey *et al.*³ using ESDIAD (Electron Stimulated Desorption Ion Angular Distribution), TDMS (Thermal Desorption Mass Spectrometry) and LEED (Low Energy Electron Diffraction). These authors concluded that cyclohexane forms, at low temperatures, a first layer of chemisorbed molecules. In this layer, the molecules are oriented essentially parallel to the surface, with three axial hydrogens directed into threefold hollow sites of the substrate. In the present work, we have investigated the adsorption of cyclohexane on Ru(001), using EELS (both in the specular and off-specular directions), angle-resolved photoelectron spectroscopy, and TDMS (combined in *one* UHV system) to investigate the orientation and symmetry of the adsorbed molecule and compare the results with the above-mentioned structural model.³

EELS measurements in the specular direction after adsorption of cyclohexane at 90 K show a C-H soft mode at 2580 cm⁻¹ (see Fig. 1), which does not increase in intensity *after* completion of the first chemisorbed monolayer.⁴ Otherwise, the vibration frequencies compare well with the gas phase vibrational modes of A_{1g}, A_{2u} and E_g, E_u symmetry (Point Group D_{3d}).² Therefore, the observation of E_g and E_u modes indicates that upon adsorption, the gas phase symmetry (D_{3d}) is reduced more than to C_{3v} or that another scattering mechanism besides small angle dipolar scattering is operative. In the case of dipolar scattering (in its strict form), the excitation of vibrational modes obeys the so-called surface normal selection rule⁵ which states that only modes with a component of the dipole moment perpendicular to the surface are dipole active.⁶ Consequently, E-modes in C_{3v} symmetry would be forbidden.

The spectrum obtained 20° off-specular⁷ in Fig. 1 clearly

shows different angular behavior for the C-H stretches at 2580 and 2920 cm⁻¹, thus indicating different scattering mechanisms. While the 2920 cm⁻¹ mode has considerable intensity off-specular due to a large angle scattering mechanism,⁸ the C-H soft mode peaks in the specular direction only, indicating forward dipole-scattering.⁹ The strong dipole enhancement observed for the C-H stretch of the first chemisorbed layer can be explained by the structural model³ mentioned previously, where three of the axial hydrogens vibrate toward threefold hollow sites of the metal substrate. The proximity of the axial C-H bonds to the metal surface can result in an interaction between the vibrating dipole and its image in the surface,¹⁰ which can cause considerable dipole enhancement and frequency shifts of the C-H stretching mode. We thus believe, based on our off-specular EELS results, that in order to explain the 340 cm⁻¹ “downshift” of the C-H soft mode, it seems unnecessary to assume hydrogen bonding with the metal surface. Furthermore, the off-specular measurements indicate that a symmetry lower than C_{3v} for the adsorbed molecule is not required to account for the ob-

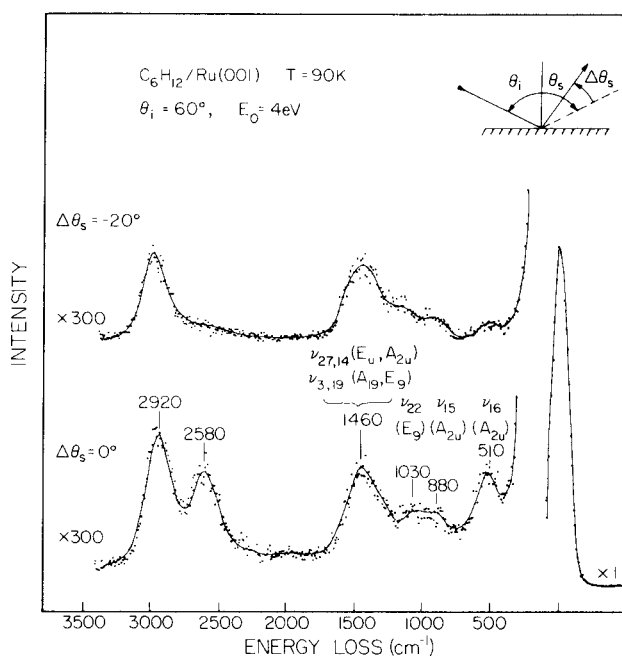


FIG. 1. Vibrational spectra of cyclohexane adsorbed on Ru(001) (90 K), obtained by EELS in the specular direction and 20° off-specular.

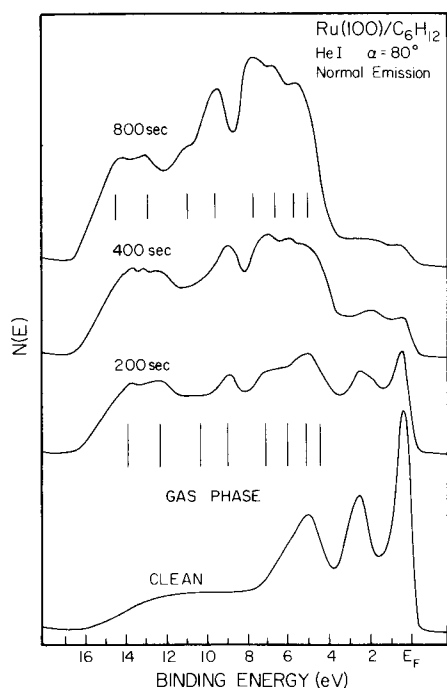


FIG. 2. Photoemission spectra for increasing exposures of cyclohexane adsorbed on Ru(001) at 90 K. The spectra were obtained in *normal* emission for HeI radiation, incident at $\alpha = 80^\circ$ from the surface normal. Exposures are in arbitrary time units of a directional beam doser.

servation of *E* modes since the corresponding modes show large angle scattering behavior which is not subject to the dipole selection rule.

In agreement with earlier measurements,¹¹ the photoemission spectra, presented in Fig. 2 for *normal* emission, compare well with the gas phase spectrum,¹² which is rep-

resented by vertical lines. Formation of multilayers occurred after large exposures (800 s), as revealed by the total suppression of the Ru *d*-band. Notice also the appearance of a peak at 11 eV which is allowed in the gas phase spectrum but symmetry forbidden for normal emission from a chemisorbed (first layer) molecule in C_{3v} symmetry. This suggests a loss of orientation for the molecules in the multilayer, which will be discussed elsewhere.⁴

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⁶ The dipole selection rule has been generally accepted for low energy electron scattering, but this rule is not so strict as in infrared due to the much smaller wavelength of the exciting electric field of the incident electron. For a more detailed discussion on this subject, the reader is referred to D. Sokcevic, Z. Lenac, R. Brako, and M. Sunjic, *Z. Physik B* **28**, 273 (1977).

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